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WASTE-DERIVED FUELS AT IRON AND STEEL MILLS AS PRODUCTS OR
WASTE FUELS, INFORMATION REQUIRED

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

JAN 24 1986

Mr. Earle F. Young, Jr.
Vice President
Energy and Environment
American Iron and Steel Institute
1000 16th Street, N.W.
Washington, D.C. 20036

Dear Mr. Young:

This is a follow up to our December 13, 1985 meeting when
we discussed the information EPA would need in order to consider
classifying the waste-derived fuels produced at iron and steel
mills as products rather than exempt hazardous waste fuels.

Our decision as to whether coke or coal tar produced from
the recycling of a listed hazardous waste, coal tar decanter
sludge, should be classified as a product rather than a waste-
derived fuel turns on whether the recycling significantly
affects to composition and, thus, the risk that coke or coal
tar may pose during transportation, storage, or use as fuel.
Specifically, we must determine whether hazardous constituents
in the recycled decanter sludge significantly increase levels
of those constituents in the coke or coal tar.

To determine whether levels of toxic organics or toxic
metals in the coke and coal tar are significantly increased by
recycling the sludge, we need triplicate analyses of the levels
of particular metals and organics (see the enclosed table) in the
coke and coal tar materials produced with and without sludge
recycling.

The metals listed in the enclosed table were selected for
evaluation because they are present in coal, and either cause
carcinogenic or other nonthreshold health effects, or are fairly
volatile, or both.

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The detection limits suggested are about an order of magnitude lower than the average levels of these metals in coal. Our concern with metals levels in the coke is that some of the more volatile metals may become concentrated in the sludge and could conceivably be reintroduced into the coker in a less volatile form, thus increasing levels in the coke product. Similarly, if volatile metals are concentrated in the sludge, mixing the sludge with the coal tar could increase metals levels.

The oraganics were selected for evaluation because they are typically produced from thermal treatment of coal, they are less volatile than phenol and napthalene already shown not to be carried over into the coke at significant levels, and they are representative of polyaromatic molecules (POMs), many of which are considered to be carcinogens. Our concern with organics in the coke is that some of the less volatile, difficult to crack POMs that are likely to be found in the sludge could conceivable be carried over into the coke product. Similarily, if POMs concentrate in the sludge, mixing the sludge with the coal tar could increase POM levels.

If you have questions, please contact Matt Straus or Bob Holloway.

Sincerely

Original Document signed

Steven Silverman
Attorney
Office of General Counsel

Enclosure

ANALYTICAL INFORMATION

(See SW-846 for description of methods.)

Metals	Method*	Detection Limit
Arsenic	6010, 7060, 7061	1 ppm
Cadmium	6010, 7130, 7131	0.1 ppm
Chromium	6010, 7190, 7191	1 ppm
Lead	6010, 7420, 7421	1 ppm
Mercury	6010, 7471	0.1 ppm

* Use acid degestion method 3050 for preparation of coal tar
  samples.

Organics	Method	Detection Limit
Anthracene/Phenanthrene	8100	1 ppm
Benzo(a)anthracene/chrysene	8100	1 ppm
Benzo(a)pyrene	8100	1 ppm
Fluoranthene	8100	1 ppm
Pyrene	8100	1 ppm
Napthalene+	8100	1 ppm
Phenol+	8040	1 ppm

+ Napthalene and phenol levels in the coke as well as the coal
  tar should be determined for comparison with previous data.

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Recycling of Hazardous Waste Materials in the Coking Process

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Every year the coking industry produces a significant amount of tarry and other wastes in byproducts plants. For the most part these wastes have not been put to any practical use. In addition, an integrated factory produces several waste oils which differ in composition and quantity, e.g., wastes from the steel rolling-mill process. In this work, the possibility of using such waste materials as binders in a partial briquetting process for metallurgical coke production is explored. By means of this coking procedure, a strong metallurgical coke not inferior in quality to coke from conventional coal blends is produced at pilot and semi-industrial scales. The use of such wastes, some of which are classified as hazardous materials, will avoid the need for dumping, thereby contributing to the protection of the environment as well as reducing the costs related to waste disposal.

Introduction

During the 1990s, coke production to feed blast furnaces in the steel industry accounted for about 320–360 Mt/year for a production of about 500 Mt/year of pig iron. This coke was produced from about 450 Mt/year of coal in approximately 250 coking plants around the world (*1*). In the year 2000, with a pig iron production of 572 Mt, coke production amounted to approximately 340 Mt (*2*).

Metallurgical coke is a carbon material that is used in the blast furnace (i) to supply the necessary heat to melt iron and slag and drive chemical reactions (an energy source); (ii) to produce and regenerate the gases for the reduction of iron oxides (a reduction agent); (iii) to provide mechanical support for the charge (a support material); and (iv) to provide a permeable bed through which reducing gases pass upward into the stack, and slag and iron droplets pass out toward the hearth of the blast furnace (a permeable material). Coke as an energy source has lost importance due to the injection into the blast furnace of some fuel, oil, tar, and specially pulverized coal (*3, 4*). Other functions, however, have also become more important for maximum efficiency in the blast furnace.

According to general opinion in the steel industry, the ironmaking route via the blast furnace will remain the basis of steel production in the foreseeable future (*5, 6*). For this reason, coke production in the world will continue to be indispensable because coke cannot be fully replaced as a raw material in the blast furnace for physical reasons (*7*).

In the coking process that uses byproducts or slot type ovens, the raw gas evolving from the coke ovens is treated to separate the permanent gases, ammonia, benzol, and tar.

At different stages of the separation process significant quantities of tar decanter sludge (TDS) and benzol distillation residue (BDR) are produced. These are estimated to be about 1000–1200 t/year and 200–250 t/year, respectively, for a coke production of about 2.5 Mt/year.

According to the U.S. Environmental Protection Agency (EPA) regulations, tar decanter sludge is classified as a hazardous waste (*8*). Modifications in coke oven operating conditions, including oven heating practice, oven charging procedure, and coal preparation conditions, have reduced the generation of tar decanter sludge. However, the problem of disposal still remains.

Environmental protection requires that coke oven plants dispose of the sludge either by recycling it internally in the process or by hauling it to an approved secure landfill. Methods for the elimination of wastes such as burial, incineration, and biodecomposition are ineffective in the case of coal-tar sludge.

At the same time, in another part of an integrated steel-making factory, 1000 t of waste lubricant oil (WLO) from steel rolling mills are produced per year (*9*).

The possibility of using these coking plant wastes by direct addition to the coal blends for coke production, without deterioration in coke quality, has been previously studied at a laboratory scale (*10*). As these waste materials are difficult to handle because the transfer chutes and coal bunkers become sticky, a new approach for recycling them is to prepare briquettes using the wastes as binders and then to incorporate the briquettes into the coke oven (*11–13*) in a process known as partial briquetting (*14*). Metallurgical coke production using partial briquetting of the charge is a well-known and widely used process, especially in Japan where about 50% of all coke produced is obtained by means of partial briquetting of the coal charge (*14*).

The use of waste lubricant oil from steel rolling mills as additive to the coal blends for the coking process, by direct addition, has also been previously studied (*9*).

In this study, the possibility of using waste material from different origins (coal-tar sludge, residue from benzol distillation column, and waste lubricant oil from steel rolling mills) as binders in the manufacture of briquettes, and then adding the briquettes to nearly 20 wt % of the oven charge for coke production is assessed as a way of helping to solve the environmental problem.

Experimental Section

Waste Materials. The main characteristics of the coking plant waste materials, tar decanter sludge (TDS) and pitch-like residue from the benzole distillation column (BDR), used for briquette production are presented in Table 1.

For the evaluation of polycyclic aromatic hydrocarbons (*15*), the carbon disulfide extracts of the coking residues and some reference materials such as an industrial tar (T) and two commercial coal-tar pitches (binder pitch (BP) and impregnation pitch (IP)) were analyzed by capillary gas chromatography (GC) using a flame ionization detector (FID). Chromatographic analyses were carried out on a Hewlett-Packard (Palo Alto, CA) model 5890 Series II gas chromatograph equipped with FID. Separations were carried out on a fused-silica capillary column of 25 m × 0.22 mm i.d. coated with OV-1701 stationary phase. The temperature was raised from 50 to 300 °C at 4 °C/min. The carrier gas used was hydrogen at a flow rate of 2 mL/min with a splitting ratio of 1:87. The temperatures of the detector and injector were 350 and 300 °C respectively, and the volume of the sample injected was 1 μL. The peaks in the chromatogram were identified by

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TABLE 1. Main Characteristics of the Materials Used

	TDS	BDR	T	BP	IP
ash (wt % db)	0.7	0.6	0.24	0.1	0.0
C (wt % daf)	92.5	89.2	91.0	94.1	93.2
H (wt % daf)	4.5	4.8	5.3	3.9	4.9
N (wt % daf)	0.9	2.5	1.1	0.9	1.2
S (wt % daf)	0.7	3.3	0.5	0.5	0.6
O (wt % daf)[a]	1.4	0.2	2.1	0.6	0.1
C/H atomic ratio[b]	1.71	1.55	1.43	1.98	1.58
coke yield[c]	32.5	35.2	13.9	44.8	38.0
TI (wt %)[d]	25.8	32.2	16.3	38.1	30.0
CS$_2$-I (wt %)[e]	21.9	37.9	12.4	37.0	26.9
softening point (°C)[f]		75		98	50

[a] By difference. [b] Carbon/hydrogen atomic ratio from elemental analysis. [c] Determined at 1000 °C in a thermobalance at 3 °C/min. [d] Toluene insoluble content. [e] Carbon disulfide insoluble content. [f] Softening point determined by the Kraemer–Sarnow method (STPTC No. PT 2-62 and UNE 7176).

TABLE 2. Characteristics of Waste Lubricating Oil (WLO) from a Steel Rolling Mill

moisture (wt %)	1.0
organic matter (wt %)	63.2
total sediments (wt %)	35.8
ash (wt %)	33.4
chloride (wt % db)	0.05
sulfur (wt % db)	0.15
nitrogen (wt % db)	0.87

comparing retention time data of available standards and data from previous studies (16).

After the raw oil was used as lubricant in the rolling process and water was removed in the plant by decantation (17), the resulting waste oil (WLO) contained mainly organic matter, sediments, and a small amount of water, as shown in Table 2.

Gieseler Plasticity Test. Coal plasticity in the coking industry is normally measured by means of the Gieseler test standardized by ASTM (procedure D 2639-74). Briefly, 5 g of a sample with a size <0.425 mm is heated while a constant torque is applied on a stirrer placed in a crucible into which the coal is charged. The maximum fluidity of the coal is expressed in dial divisions per minute (ddpm).

Coal Blends. The coal blends labeled A and B were prepared and supplied by the Spanish Steel Company. Coal blends are prepared monthly by the company to obtain similar characteristics, by mixing bituminous coals of different rank, thermoplastic properties, and geographical origin (Australia, Canada, Poland, and the United States). In the present case, the main average characteristics are as follows: ash = 7.6 wt % db, volatile matter = 25.5 wt % db, S = 0.72 wt % db, Gieseler maximum fluidity = 918 ddpm.

Briquettes Production. Three series of briquettes were produced using a pilot roll-press available at INCAR (13). The press is two rollers of equal diameter running in opposite directions at the same speed. The compaction was carried out by squeezing the material through the gaps between the two rollers. The coal and residues were mixed and stirred in a bunker heated with steam until the blend reached 80 °C. The mixture was then fed between the rollers by a distributor pan. The briquettes obtained had an ellipsoidal shape with a 55 and 50 mm length axis and a weight of around 22 g. Briquettes were produced using the three types of waste materials and the coal blends. The coal blends were ground to a particle size nearly 80 wt % less than 3 mm, the same particle size as for coal blend carbonization and avoiding any special preparation procedure.

Carbonization Tests at Pilot Scale. Carbonization tests of the coal blends and the mixtures of the coal blend with

briquettes at pilot scale were carried out in a movable wall oven (MWO) of 250 kg capacity. The oven dimensions were 1 m length, 1 m height, and 0.456 m width. The oven has silicon carbide refractory walls with high thermal conductivity and was electrically heated. The initial temperature was 880 °C, which was raised to 1132 °C at a rate of 14 K/h, resulting in a carbonization time of 18 h. The coke was pushed from the oven and quenched with water. The coal blend used, as in the case of the production of briquettes, was ground to a particle size nearly 80 wt % less than 3 mm.

Carbonization Tests at Semi-Industrial Scale. Carbonization tests at semi-industrial scale were carried out in the 6-t capacity oven of the INCAR Experimental Coking Plant (18). The dimensions of the oven are 2.8 m height, 6.5 m length, and 0.45 m width. The coking time was 18 h and the mean flue temperature was around 1230 °C. The coke was pushed from the oven and was quenched with water. The results obtained from semi-industrial scale carbonizations apply directly to industrial scale.

Coke Quality. Coke cold mechanical strength was evaluated by the Irsid test according to the ISO 556 standard procedure. In this test, 50 kg of coke not able to pass a round-hole sieve of 20 mm was subjected to 500 revolutions in a standardized drum and afterward sieved. Two indices, I20 and I10, were obtained from this test. The I20 index was the weight percent of coke remaining above 20 mm in size and gives the extent of coke cohesion The I10 index, which was the weight percent of coke obtained below 10 mm in size, was used to assess the abrasion resistance of the resultant cokes. The higher the I20 and the lower the I10, the better the coke quality. The two Irsid indices are widely used to indicate the strength of coke from full-size coke ovens.

Coke reactivity toward CO_2 (CRI index) and coke strength after reaction (CSR index) were assessed by the CRI/CSR test developed by the Nippon Steel Corporation (NSC) and standardized afterward by ASTM (procedure D5341). Briefly, a sample of coke (200 g) with a particle size between 19 and 22.5 mm was made to react at 1100 ± 5 °C for 2 h with CO_2 at a flow rate of 5 L/min. The coke residue was weighed and subjected to the tumbler test. The CRI was calculated as the percentage of weight loss. The mechanical degradation of the residue after CO_2 reaction (CSR) was measured as the weight percent of coke larger than 9.5 mm size after the drum was rotated 600 times at 20 rpm and the coke was sieved through a 9.5 mm sieve. As is well-known, the lower the CRI and the higher the CSR, the better the quality of the coke.

Results and Discussion

Origin and Characterization of Waste Materials. Table 1 shows the main characteristics of the TDS and BDR accumulated during different periods of time. For comparison purposes, an industrial tar (T) and two commercial coal-tar pitches, binder (BP) and impregnation (IP), are included.

All the waste material is mainly composed of about three-quarters of a soluble fraction in organic solvents. The relative abundance of soluble and insoluble fractions depends on the operation conditions and can be expected to play an important role in the thermoplastic behavior of a coking coal or a coking blend. The soluble fraction should also act as a binding component similar to commercial tars and pitches, while the insoluble fraction will act as a poorly caking filler component. In agreement with the solubility parameters (TI and CS$_2$-I), the coke yield determined in a thermobalance at 1000 °C is slightly higher for the residue from the benzol distillation column: 35.2 wt % versus 32.2 wt % of the tar decanter sludge. The lowest coke yield corresponds to the tar (13.9 wt %) which also has the lowest amount of insoluble material in organic solvents. The highest coke yield corresponds to the binder pitch (44.8 wt %) which has the highest

TABLE 3. Content of 16 PAHs Classified as Hazardous by the U.S. Environmental Protection Agency (EPA) Expressed as Wt %

PAH	TDS	BDR	T	BP	IP
naphthalene	5.20	0.00	7.20	0.16	0.11
acenaphthylene	2.24	0.27	2.52	0.00	0.00
acenaphthene	0.09	0.26	0.26	0.18	0.28
fluorene	0.92	0.84	1.23	0.13	0.14
phenanthrene	4.94	3.42	5.46	0.51	0.23
anthracene	0.97	0.78	1.09	0.08	0.04
fluoranthene	4.06	2.72	4.15	0.86	0.47
pyrene	3.10	2.08	3.11	0.92	0.47
benzo[a]anthracene	1.13	0.87	1.15	0.59	0.33
chrysene	1.05	0.93	1.23	0.90	0.51
benzo[b]fluoranthene	0.88	0.79	0.88	0.76	0.41
benzo[k]fluoranthene	0.37	0.26	0.34	0.18	0.10
benzo[a]pyrene	1.15	0.93	1.05	0.98	0.46
dibenzo[a,h]anthracene	0.16	0.19	0.17	0.18	0.12
indeno[1,2,3-cd]pyrene	0.85	0.78	0.76	0.88	0.33
total 16 EPA PAHs (mg PAHs/g additive)	2.711	1.512	3.060	0.731	0.400

TABLE 4. Composition of the Briquettes Expressed as Wt %

	coal blend	TDS	BDR	WLO
briquettes 1	85.0	12.5	2.5	
briquettes 2	83.5	12.5	2.5	1.5
briquettes 3	84.5	12.5	2.5	0.5

TABLE 5. Parameters Derived from the Gieseler Fluidity Tests

	T_s (°C)	T_f (°C)	T_r (°C)	$T_r - T_s$ (°C)	MF (ddpm)
coal blend A	399	450	492	93	972
briquettes 1	360	449	499	139	14665
briquettes 2	388	453	489	101	855

amount of toluene insoluble materials. It was found that, except for BDR and IP, the higher the coke yield, the higher the toluene insoluble material. Tar (T) presents the lowest C/H, followed by the residue from the benzol distillation column (BDR), impregnating pitch (IP), tar decanter sludge (TDS), and binder pitch (BP). The C/H atomic ratio gives an indication of the aromaticity of the waste material. In the present case, the residue from the benzol distillation column that has the lower C/H ratio has a higher content of insoluble material in organic solvents. This can be attributed to the different origin of the additives and, consequently, to the different nature of the constituents of the insoluble fraction (10). As regards the ash content, an important parameter when considering its addition to a coal blend for cokemaking, it is very low in both cases, and, as will be seen later, will compensate the higher ash content of the WLO, thus minimizing its possible deleterious effect on coke quality. The Kraemer–Sarnow softening points (STPTC PT 2-62 and UNE 7176) of the impregnation and binder coal-tar pitches are 50 and 98 °C, respectively; that corresponding to the pitch-like residue (BDR) is in the middle of the two, at 75 °C.

The hazardous nature of these wastes was evaluated by using the amounts of the 16 PAHs classified by the U.S. Environmental Protection Agency (EPA) as priority pollutants.

The amount of each individual PAH and the total amount of the 16 PAHs per 1 g of waste to be used as coking additive is given in Table 3. TDS is very similar to the industrial coal-tar (T), with the lighter PAHs such as naphthalene, phenanthrene, fluoranthene, and pyrene being the most abundant. The total amount of the EPA PAHs is 2.711 mg/g TDS and 3.060 mg/g tar. In the case of BDR the three highest PAHs correspond to phenanthrene, fluoranthene, and pyrene, with the total amount of EPA PAHs being 1.512 mg/g BDR. For the binder coal-tar pitch (BP) the total amount of EPA PAHs is 0.731 mg/g BP, with the heavier PAHs benzo[a]pyrene, chrysene, and pyrene being the most abundant. With respect to the impregnation coal-tar pitch (IP) the most abundant individual PAHs are fluoranthene, pyrene, and chrysene and the total amount of EPA PAHs is 0.400 mg/g IP. An examination of the EPA PAHs reveals that BDR is more similar in composition to an impregnation pitch than to a binder coal-tar pitch and it can be considered more hazardous than any of the two commercial coal-tar pitches. Taking into account the PAHs analysis, TDS can be considered a more hazardous waste than BDR.

WLO is used to lubricate rolled plate in the tandem mill. First, it must be emulsified with water which, once used, is removed (17). Table 2 shows the chemical composition of WLO after water removal. It was found to be composed mainly of organic matter (63.2 wt %) accompanied by sediments of an organic and inorganic nature (35.8 wt %) and 1 wt % of water. The sediments are made up mainly of ashes (33.4 wt %), with the main component being iron oxide (9). The composition of the ashes is important because of the catalytic effect of certain minerals on the CRI index, and thus on CSR because of their linear relationship, i.e., the lower the reactivity to CO_2 (CRI), the higher the coke strength (CSR).

Carbonization Tests. The first approach to recycling WLO was its direct addition to an industrial coal blend (9). Additions of 0.5 and 1 wt % of WLO to an industrial blend produces slight increases in the ash content, and the bulk density of the coal charge in the oven, without the deterioration of the coke quality parameters. Previous research work (10) was carried out to evaluate the utilization of hazardous wastes from the byproducts of coking plants such as TDS and BDR in the production of metallurgical coke. The effect on coke quality was related to the ability of the wastes to modify the system during the plastic stage.

As stated above, these waste materials are difficult to handle. Thus, their use as binders to produce briquettes could be a possible solution for their disposal. The partial briquetting of a coal charge before coking is an effective process that ensures a significant reduction in the amount of good-coking coals in coke ovens with the simultaneous stabilization and improvement of the physical and chemical properties of the coke. The process consists of briquetting part of the coal charge with a binder, mixing the briquettes with the unbriquetted charge, and coking the blend obtained. The process is fairly simple and reliable, and it can be incorporated easily into an existing coke oven plant.

The composition of the briquettes shown in Table 4 was optimized to consume nearly the equivalent to the amount of TDS and BDR produced annually by a medium-size coking plant, i.e., briquettes 1 which contain 12.5 wt % of TDS and 2.5 wt % of BDR. However, the amount of WLO in the briquettes must be carefully controlled because of its high iron oxides content, which represent more than 90 wt % of the ashes, and the catalytic effect of the coke gasification reaction, and so it was added as a minor component. Briquettes 2 and 3 together with TDS and BDR contained waste lubricant oil from the steel mills in amounts of less than 1.5 wt %. The total amount of waste materials in these briquettes is 16.5 and 15.5 wt %, respectively. Gieseler fluidity test of the coal blend A and briquettes 1 and 2 was carried out, and parameters derived from the test are included in Table 5. Briquettes 1, containing fluidity enhancers (BDR and TDS), show an important increase in maximum fluidity and plastic range (difference between the resolidification temperature, T_r and the softening temperature, T_s) with respect to the base coal blend (14 665 vs 972 ddpm and 139 vs 93 °C, respectively). This ability of BDR and TDS to modify the plastic stage of a coal is in agreement with previous results

TABLE 6. Main Characteristics of Coal Blend, Coking Conditions in the 250-kg Movable Wall Oven, and Coke Characteristics

	coal blend A	coal blend A + 20 wt % briquettes 1	coal blend A + 20 wt % briquettes 2
moisture (wt %)	10.2	9.0	7.2
ash (wt % db)	7.8	7.6	7.7
VM (wt % db)[a]	26.0	26.8	26.5
S (wt % db)	0.73	0.75	0.74
bulk density (kg/m^3 db)	653	697	721
coking time (h)	18	18	18
Coke Characteristics			
ash (wt % db)	10.8	10.3	10.4
VM (wt % db)[a]	0.1	0.1	0.3
S (wt % db)	0.70	0.71	0.71
I20 (wt %, >20 mm)	67	74	75
I10 (wt %, <10 mm)	30	24	23
CRI (wt %)	28	28	27
CSR (wt %, >9.5 mm)	53	58	57

[a] Volatile matter content.

TABLE 7. Main Characteristics of Coal Blend, Coking Conditions in the 6-t Oven, and Coke Characteristics

	coal blend A	coal blend A	coal blend A + 20 wt % briquettes 1
moisture (wt %)	10.3	8.7	6.9
ash (wt % db)	7.8	7.8	8.4
VM (wt % db)[a]	26.0	26.0	26.7
S (wt % db)	0.73	0.73	0.72
bulk density (kg/m^3 db)	723	748	756
coking time (h)	18	18	18
mean flue temperature (°C)	1242	1249	1248
Coke Characteristics			
ash (wt % db)	10.6	10.5	10.5
VM (wt % db)[a]	0.5	0.1	0.3
S (wt %)			
I20 (wt %, >20 mm)	74	75	75
I10 (wt %, <10 mm)	23	22	22
CRI (wt %)	25	26	25
CSR (wt %, >9.5 mm)	62	62	64

[a] Volatile matter content.

(10, 15) obtained from direct additions to a coking coal. Briquettes 2, which contain BDR and TDS and the residue from a lubricant oil (WLO, which was shown previously to contain a high amount of mineral matter) produce a slight increase in the plastic stage of coal, but do not increase the maximum fluidity of the blend. Also, the amount of water of WLO seems to be important when considering its ability to modify the plastic stage of the coal blend. To avoid the variability in the composition of the briquettes, three were used as starting material for the test. However, taking into account that to carry out Gieseler fluidity measurements (ASTM D-2639-74), the briquettes must be converted into a blend of coal and residues with a specific particle size distribution, the differences in plastic parameters should be taken with caution.

The main characteristics of coal blend A (a typical coal blend used by the Spanish steel industry) and its mixtures containing 20 wt % of briquettes 1 and 2 are shown in Table 6. Coking conditions in the 250-kg movable wall oven and coke quality data are also included. It can be clearly seen that the incorporation of these briquettes to coal blend A increases the bulk density of the charge. The quality of the coke is also improved, with the extent of the improvement in Irsid indices, I20 and I10, being of the order of 7 and 4 points, respectively. Coke reactivity to CO$_2$ (CRI) is similar when comparing cokes with and without the addition of briquettes, but coke strength after reaction (CSR) is better in the case of cokes prepared with waste addition. It is well-known that there is a linear relationship between CSR and CRI (19–21). Nevertheless, it has to be taken into account that this type of correlation was obtained with cokes produced at an industrial scale where operational conditions such as bulk density are maintained almost constant. When dealing with cokes produced at a pilot scale, variations in bulk density are common and produce a clear effect on CSR with no variation of CRI (22). Coking experiments carried out with the same blend and different bulk densities give rise to similar values of CRI and increasing values of CSR according to the increasing bulk density of the coking test.

The favorable effect of an increase in bulk density by small additions of oils on coke mechanical strength is well-known (23). However, coke quality improvement when briquette-blended charges are carbonized is considered to be also the result of the presence of tar- and pitch-like materials in the charge. Additives such as tar and pitch, commonly referred to as fluidity enhancers, modify the most important stage in the transformation from coal to coke. As coal is heated in an inert atmosphere, it undergoes depolymerization and decomposition, resulting in the evolution of gas and condensable vapors and the formation of a solid residue with a high carbon content. Certain coals, therefore, soften and become plastic upon heating, coalescing to form a coherent fluid mass before finally resolidifying. It is during this stage (plastic stage of coal, 350–550 °C) that the main features of coke structure, porosity, and pore-wall structure, are formed. Similarly, tar and pitch-like additives, on carbonization, soften at temperatures below or within the plastic temperature range of a coking coal, thereby increasing the maximum fluidity and the plastic temperature range of the system. Thus, the ability of an additive to interact with coal in the plastic stage of the co-carbonizing system determines the efficacy of the additive in the formation of an adequately bonded structure in coke, improving coke strength (9, 15, 24). Therefore, additions of fluidity enhancers such as TDS and BDR, are more effective when used as binders in briquette production than when added directly (23). The effect of the use of waste materials as modifiers of the reacting system against bulk density has been previously studied (25) by comparing the results of the co-carbonization tests of two charges, one of which contained briquettes made up of waste materials (TDS and BDR), the other corresponded to the base blend with bulk density similar to that of the charge containing briquettes. Bulk density of the two tests was 762 kg/m^3 db for the charge with briquettes versus 772 kg/m^3 db for the reference charge of coal blend. There was a positive effect on coke quality parameters due to the presence of waste materials. The briquette-blended charge produced a slight increase in the coke cohesion (I20), decrease in coke abrasion (I10), and a slight improvement in CRI value with no variation of CSR.

To better clarify the importance of the two effects taking place, i.e., bulk density improvement due to briquettes addition and effect of tar and pitch-like additives in the charge, three coking tests were carried out at a semi-industrial scale. Two of the tests were performed using the base coal blend at two different bulk densities and the other used a partially briquetted charge and a bulk density similar to one of the tests carried out with the base blend. Table 7 shows the coking conditions together with coke quality data. Although a slight improvement in CSR has been observed, the addition of pitch-like material as binder to form the briquettes does not have a clear effect in cold mechanical strength (I20 and I10 indices). Therefore, the effect of briquettes on coke quality can be

TABLE 8. Main Characteristics of Coal Blend, Coking Conditions in the 6-t Oven, and Coke Characteristics

	coal blend B	coal blend B + 15 wt % briquettes 3
moisture (wt %)	11.4	9.6
ash (wt % db)	7.4	7.8
VM (wt % db)[a]	24.9	25.4
S (wt % db)	0.72	0.74
bulk density (kg/m³ db)	740	750
coking time (h)	18	18
mean flue temperature (°C)	1230	1235
Coke Characteristics		
ash (wt % db)	9.9	10.2
VM (wt % db)[a]	0.2	0.1
S (wt % db)	0.68	0.71
I20 (wt %, >20 mm)	75	78
I10 (wt %, <10 mm)	22	20
CRI (wt %)	25	26
CSR (wt %, >9.5 mm)	62	62

[a] Volatile matter content.

considered a combination of the two effects derived from, on one side, an increase in the bulk density of the charge and from the incorporation of the tar and pitch-like residues as binders in the briquettes. On the other hand, briquetting also leads to a change in the physical characteristics of coal charges and consequently to a change in the conditions of heat and mass transfer. There is a significant decrease in the distance between the reacting particles, which increases the rate of polycondensation of the residual products resulting from the destruction of coal organic matter.

To confirm the feasibility of adding briquettes containing the three types of wastes to an industrial coal blend via a partial briquetting process, additional semi-industrial tests were carried out in a 6-t oven. Carbonizations were performed on the industrial coal blend B with a 15 wt % addition of briquettes 3. The temperature of the heating walls was maintained at 1230 and 1235 °C during the test without and with briquettes addition, respectively; the bulk density is 10 kg/m³ higher when briquettes are added (Table 8). The effect of the addition of briquettes slightly modifies the characteristics of the coal blend (Table 8).

Coke quality produced with briquettes addition is of a slightly better quality in terms of cold mechanical strength (Irsid indices, I20 and I10) and without variation, if the hot coke properties, CRI and CSR indices, are considered. Coke quality data (Table 8) confirm the results obtained in the 250-kg oven, although in this case there is no change in hot coke strength (CRI/CSR index) with the addition of briquettes 3. Two factors have to be considered: (a) not much bulk density increase due to briquettes addition was attained, and (b) the composition of the briquettes. Briquettes 3, apart from fluidity enhancers (BDR and TDS) that could have a positive effect on CSR, contain WLO with a high mineral matter content that can catalyze coke gasification reaction; thus, having a deleterious effect on CRI and CSR. However, the negative effect is not clear due to the small amount of WLO in the charge of the oven, 0.5 wt % in the briquettes represents less than 0.1 wt % in the charge. It can be deduced, therefore, that it is possible to recycle different types of hazardous wastes from the byproducts plant of a coking industry as binders for briquette manufacture. It was also proven that it is possible to incorporate into the briquettes other types of residues such as waste lubricating oils from a different part of an integrated steel-making factory.

The benefits of using the residues in situ, to produce briquettes that will be used in the production of coke are both economic and environmental. With this scheme of briquettes and residues production, it will be possible, charging two ovens of the industrial battery with a partially briquetted charge containing 20 wt % of briquettes during a month, to eliminate the wastes produced in a month. Moreover, the benefits lay not only in the savings of coal, but in the fact that this procedure avoids transport and disposal costs of a type of wastes highly hazardous for the environment. The next step will be a full-scale test to confirm the results presented in this work. From the point of view of the steel-making industry, the implementation of such a procedure will bring economic and environmental benefits without impairment of coke quality.

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